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HIGH-MELTING HEAT-INSULATING MATERIALS OBTAINED BY FOAMING AND GASSING METHODS

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Heat-insulating ceramic materials have been developed, whose porous structure is provided by foaming and gas formation. Foaming and gas-forming agents, stabilizing, plastifying, and other additives and fixing agents for foam and gas mixtures are identified.

Heat-insulating materials and products are used in various sectors of the industry to insulate heat-generating equipment, which helps to reduce heat losses via the ambient medium and leads to saving fuel and energy.

There is no production of high-melting and refractory heat-insulating materials in Belarus; such materials are imported from abroad. Therefore, the use of available raw materials from Belarus (high-melting clay, kaolin, carbonate rocks, inexpensive fuel resources) for the purpose of producing heat-shielding materials is technologically justifiable and economically expedient.

The purpose of the present study was to develop mixture compositions and processes for producing high-melting ceramic heat-insulating materials using raw resources from the Belarus Republic.

A distinctive property of heat-insulating materials and articles is their high porosity, which significantly lowers their thermal conductivity. A great effect on thermal conductivity is exerted by the type of porous structure, the size, and the shape of pores. The best heat-insulating capacity is registered in materials with sealed spherical pores [1]. As the pore size increases and they transform into open channels, the heat-shielding properties deteriorate. Therefore, the aim is to develop heat-shielding materials with a uniformly distributed fine-pore structure, in which the direction of heat flow has an insignificant effect on the variation of the thermal conductivity of the material and which increases the strength of highly porous articles. The pore shape in real materials in most cases differs from the spherical shape, which is the reason for anisotropy of thermal conductance and strength.

Heat-insulating materials are produced using different methods to form a porous structure, but the most suitable for industrial production are the methods of foaming and gas formation, as well as the burn-out additive method [2].

The main disadvantage of the burning-out additive method is the restriction imposed on the upper limit of porosity (65%). This is due to the fact that burning-out additives after burning form pores of irregular shapes, which create high stresses in the material under loading. Therefore, the strength of the article decreases with increasing amount of the additive and does not ensure the prescribed mechanical characteristics in the material [1]. In order to obtain a highly porous structure in heat-insulating materials, it is recommended to use the methods of foaming and gas formation.

The foaming method consists in mixing the pororized material with a preliminary obtained foam, whose stabilized bubbles are the air pores of the heat-insulating material. The foam is obtained by whipping (intense stirring) a mixture consisting of water, a foaming agent, a foaming activator, and a foam stabilizer in blade mixers. In some cases other correcting additives are introduced.

A glue-colophony foaming agent is the most widely used in the industry [3, 4]. It yields a high amount of stable foam. Its disadvantages include the need for protracted whipping of the emulsion to provide foam and loss of the properties of the emulsion in long-time storage.

The foam in the present study was obtained using the IS-1 foaming agent (based on aminol with additives) and, for reference purposes, the PK glue-colophony foaming agent. The foam stabilizer was aluminum sulfate and a 10% solution of polyvinyl alcohol. Adding PVA into the suspension with the stabilizing additive of aluminum sulfate not only decreases the density of foam mixtures but also increases their aggregate resistance [3].

It was experimentally found that the yield of the foam volume depends on the type of foaming agent and the agitation intensity. The foaming capacity of the IS-1 agent is significantly higher than that of glue-colophony. Thus, in the first case a 7 – 10-time increase in the foam volume is regis-

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tered after 2–4 min of agitation, whereas in using the PK foaming agent, one requires a longer time of agitation with a lower foaming ability.

The structure of the foam obtained using the IS-1 foaming agent is more homogeneous; therefore, this agent was chosen for further studies. The foam was produced on the basis of an emulsion containing liquid (water), the IS-1 foaming agent, $\text{Al}(\text{SO}_4)_3$ and a 10% solution of PVA. The foaming duration was 2–4 min. The multiplicity of foam was 7–9.

The foam exhibited good froth resistance and elasticity, its density was 40–60 kg/m³, and the average bubble size was 1–3 mm. The suspension used had a density of 1680–1700 kg/m³.

When heat-insulating materials are produced by the gassing method, certain compounds are introduced in a suspension of the pororized matrix, which enter into chemical reactions accompanied by gas emission providing for the porous structure of the material. This method of pore formation has found extensive application in making cellular binders (for instance, concrete). The chemical gassing methods are infrequently used in ceramic technology. The present study considered the reactions between carbonates and acids, which is the most ideal; these reactions produce carbon dioxide CO_2 , which makes the ceramic matrix porous. Sulfuric acid was used for the gassing reaction.

The materials that are rendered porous in the production of heat-insulating articles can contain various components, whose selection is determined by the final properties of the product. We used chamotte (waste refractory product), high-melting clays from the Gorodnoe (Brest Region), and Gorodok (Gomel Region) deposits, and dolomite from the Ruba deposit (Vitebsk Region).

Fixing and mineralizing additives are introduced in mixtures in order to increase the stability of pororized mixtures, accelerate the drying of molded pieces, prevent their cracking, and impart a certain mechanical strength [5]. The size of the filler grain corresponded to the fraction below 0.5 mm in foaming and to below 0.2 mm in gas formation [6].

Gypsum was chosen as the fixing agent in mixtures rendered porous, since materials with a higher tendency to formation of coagulation structures (carboxymethylcellulose, clay, or bentonite) did not provide for the desired intensity of curing and strengthening of the samples. The gypsum content varied from 5 to 15%. In order to accelerate the curing and strengthening of samples, the experimental foam mixtures included a mineralizing additive consisting of a mixture of portland cement and low-roasted kaolin or refractory clay in the ratio of 3 : 1.

The density of the ceramic suspension was controlled by adding water, which amounted to 28–34% in foaming and 32–37% in gas formation.

The porous structure of heat-insulating materials to a large extent determines the respective level of the physico-chemical properties. Therefore, to obtain articles with pre-

scribed service properties, such as heat resistance, thermal conductivity, and durability, it is necessary first of all to control their structure, i.e., the size and the distribution of pores, their shape, and the total quantity.

It is known that the density of the obtained foam materials depends on various factors, primarily, on the density of suspensions, the ratios of the foam and suspension quantities, the amount and type of stabilizing additive, and the foam density. The foam material density decreases in proportion to the amount of foam, but the best parameters are achieved when the ratio of the volumes of foam and suspension $V_f : V_s$ is equal to 5–10 [7].

However, the authors of [6] experimentally demonstrated that the overall porosity in the case of the spherical cell shape in a foam material can reach 80.73%. Taking into account the moisture, which decreases in drying of the foam mixture, the overall porosity of a dried piece can reach 95–97%. This makes it possible to assume that even in producing the lightest foam ceramics, the multiplicity of foam mixtures, i.e., the ratio of the foam volume to the volume of the initial suspension, does not exceed 5; in this case the cells can be considered as strictly spherical, which correlates with the minimum free surface of the system [8]. Based on the above, the ratio of $V_f : V_s$ was taken equal from 2 : 1 to 5 : 1.

In preparing foam mixtures it was established that an increase in the foam content degrades the quality of mixing. To achieve a homogenous suspension, it was necessary to extend the duration of mixing. In this case the capacity of the mixture to solidify within the limits of a prescribed technological time deteriorated, and the strength of molded pieces decreased. As the amount of foam varies, the macrostructure is modified. With a low foam content the samples have a cellular matrix structure with a continuous solid phase. The pores of the material are sealed and have a virtually spherical shape, and as the porosity grows, the pore geometry changes and they transform into irregular polygons. The pore wall thickness decreases with growing porosity, since the degree of cohesion of the solid phase decreases, and the content of pores in the form of sealed cells is diminished. Furthermore, a tendency for obtaining a fine-pore structure is observed. In some compositions, sedimentary stratification of the foam mixture was observed, i.e., lower porosity in the bottom part of the sample and a well extended pore structure in the upper part.

The preparation of mixtures for swelling consisted in thorough mixing of dry batch components, after which heated water and electrolyte were added to the mixture. For a fast process, the temperature of the water should be 40–50°C. The resulting slip was thoroughly mixed, and then a premeasured quantity of concentrated sulfuric acid was added to the slip. The mixture was quickly agitated and after the beginning of swelling it was poured into detachable metal molds. The duration of gassing did not exceed 5–7 min and the total interval of the chemical reactions lasted 12–15 min. The effect of “settling” along the height

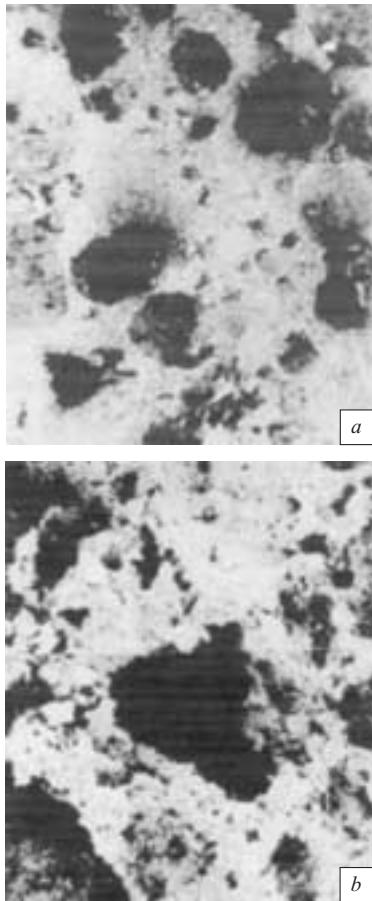


Fig. 1. Structure of heat-insulating materials produced by foaming (*a*) and gassing (*b*) methods.

of the sample was registered in both the gas mixtures and the foam mixtures.

The samples produced by both methods were dried in molds. Final drying was performed outside the molds. The compositions that had a uniform cellular structure and satisfactory strength after drying were chosen as the optimum ones. The samples were fired at temperatures of 1160–1200°C with 1-h exposure at the maximum temperature. The fired samples were visually inspected to assess their quality and subjected to testing to check their compliance with the imposed requirements.

The electron microscopic study of the structure of the heat-insulating materials obtained from foam mixtures demonstrated that the solid matrix (skeleton) has a homogeneous granular macrostructure based on light-colored fused grains, which presumably belong to refractory chamotte, cemented by an amorphous material representing a solidified vitreous phase, which is formed as a result of melting of low-melting glass components under firing and the emergence of low-temperature eutectics. The pores against the background of the matrix, as a rule, have a spherical shape and are separated, i.e., sealed (Fig. 1*a*). Such a structure is observed in the photos of the external surface of the samples

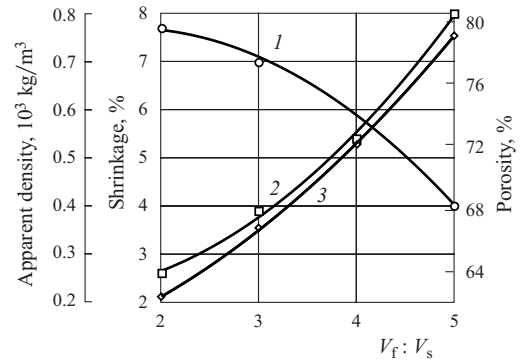


Fig. 2. Density (1), porosity (2), and shrinkage (3) of a foam material versus the foam content.

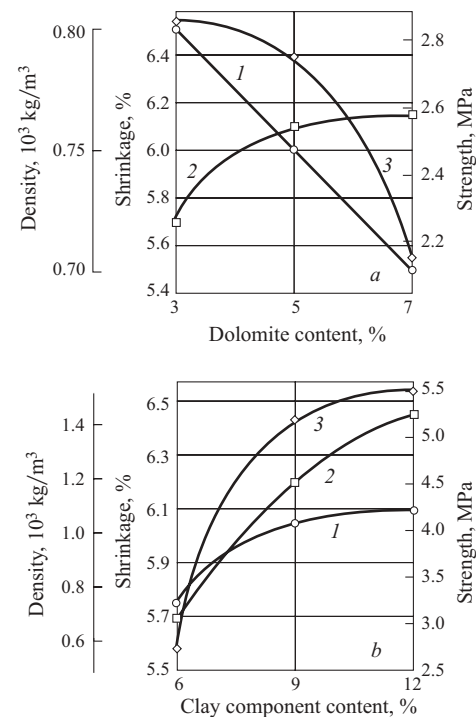


Fig. 3. Density (1), porosity (2), and strength (3) of a gas material versus the content of dolomite (*a*) and the clay component (*b*).

and of the fractures. The pore sizes vary from 200–300 μm to 2–3 mm. Large spherical pores prevail in the samples obtained.

The structure of gas lightweight materials is heterogeneous, which is usually typical of these materials. The porosity of the samples is substantial, the pore volume is 50–70%. Sealed and communicating pores are both registered. The pore configuration is irregular. A substantial spread is observed in the pore size, from very small spherical pores with a diameter less than 0.05 mm to large elongated pores up to 3.5–4.5 mm. The distribution of pores along the height of the sample is nonuniform, which can be seen in the photos of the lateral surfaces (Fig. 1*b*).

TABLE 1

Parameter	Existing materials (GOST 5040-96)		Newly developed materials	
	ShL-0.9	ShTL-0.6	foam lightweight	gas lightweight
Apparent density, kg/m ³	≤ 900	≤ 600	600 – 700	700 – 800
Thermal conductivity, W/(m · K)	≤ 0.4	≤ 0.25	0.25 – 0.32	0.34 – 0.40
Compressive strength, MPa	≥ 2.5	≥ 2.5	2.5 – 3.5	2.6 – 2.9
Additional linear shrinkage, %, not greater than, at a temperature of:				
1270°C	≤ 1	–	–	0.8 – 0.9
1150°C	–	≤ 0.7	0.6 – 0.7	–

The obtained data substantiate the possibility of using the foaming and gassing methods to make highly porous heat-insulating materials, whose porosity can be controlled, and thus to control their main properties.

It is established that under the optimum ratio of $V_f : V_s$ equal to 3 – 4 it is possible to obtain a foam lightweight material with apparent density $(0.58 – 0.70) \times 10^3$ kg/m³, porosity 66 – 72%, and fire shrinkage 3.5 – 5.5% (Fig. 2).

Since foam-ceramics is used in construction, their compressive strength was analyzed. The strength of the samples varies within rather wide limits (2.3 – 5.0 MPa) and depends on the pore structure of the sample. As the diameter of the pores and the overall porosity increase, the sample strength decreases, and as a consequence, the samples have identical mechanical strength in spite of certain differences in the content of foam in the materials. In general the minimum strength values were registered under the maximum foam content. An increase in the degree of sintering increases the strength of the samples.

In gas lightweight materials a more substantial spread in the properties was observed than in foam materials. The apparent density varied within the range $(0.7 – 1.1) \times 10^3$ kg/m³, and the porosity was 56 – 72%. The total shrinkage of the material (mostly air shrinkage) in all samples was close: from 5.6 to 6.6% (Fig. 3a).

The replacement of a part of chamotte with clay caused an increase in the average density of the samples and the prevalence of pores less than 0.3 mm in diameter, which was probably due to the plastifying capacity of clay particles, but at the same time the sinterability of the samples improved, and accordingly, their strength increased (Fig. 3b).

The thermal conductivity of porous heat-insulating ceramics is the main property determining its application areas.

It is established that the thermal conductivity of the experimental samples at 350°C ranges within the limits 0.25 – 0.55 W/(m · K). As the $V_f : V_s$ ratio grows, the thermal conductivity of the foam mixtures regularly drops, but this dependence is not linear.

The properties of the optimum compositions of the materials developed are listed in Table 1.

Thus, heat-insulating ceramic materials whose porous structure is provided by foaming and gas formation have been developed on the basis of raw materials from the Belarus Republic. In spite of a certain spread in the analyzed properties, the optimum material compositions and their production technologies allow for achieving a rational combination of these properties within the permissible limits defined by the existing standard.

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